REMARKS/ARGUMENTS

The application has been amended. In particular, claim 1 has been amended to recite that the deposition of the metal is conducted on the surface of the ion-exchange resin product and inside the resin product. Support for this amendment can be found in the application as filed on page 20, lines 10-15. In addition, new dependent claims have been added which define the thickness of the metal electrode formed on the ion-exchange resin product. Support for such language can be found in the application as filed on page 14, line 22 through page 17, line 7. As such, none of the amendments are considered new matter within the meaning of 35 U.S.C. §132. In view of the amendments above and the remarks below, entry of the amendment and reconsideration are respectfully requested.

Claims 1, 8, and 9 stand rejected under 35 U.S.C. §103(a) as being unpatentable over Shahinpoor et al., WO 97/26039, considered alone or in combination with U.S. Patent No. 4,364,803 to Nidola et al. This rejection is respectfully traversed.

The present invention is directed to a process for producing an actuator element involving forming metal electrodes on an ion-exchange resin product through repeatedly conducting the sequential steps of adsorption, deposition, and washing. The claims require repeatedly conducting these steps, such that the metal electrode is deposited on the surface of the ion-exchange resin product and inside the resin product. By depositing the metal on the inside of the resin product, the contact area between the ion exchange resin product and the metal electrode increases, which increases the quantity of ions migrating to the electrode. This results in a high degree of bending or displacement of the electrode, thereby providing quick response for the electrode. Deposition of the metal on the inside of a resin product is not taught or suggested by the prior art, let alone the high degree of bending/displacement achieved through such a deposition process in which the metal is deposited inside the resin product.

In particular, the Shahinpoor and Nidola references, whether considered alone, or in combination, fail to disclose or suggest deposition of the metal not only on the surface, but also inside the resin product, as achieved by repeatedly conducting the adsorption, deposition, and washing steps. It has unexpectedly been discovered through the present invention that repeatedly conducting such steps will cause the metal to be deposited within the interior portion of the resin, and that such an improved electrode achieves increased

bending and displacement. In fact, the Shahinpoor and Nidola references expressly teach away from such a process in which the metal is deposited in the interior of the resin.

Shahinpoor merely discloses a method for creating an actuator through reduction on an ion-exchange material. At most, Shahinpoor teaches that a reducing and rinsing step can be repeated. It is noted, however, that Shahinpoor merely teaches deposition on the surface of the membrane, and fails to describe deposition of the metal in the interior of the resin. Page 13 of Shahinpoor specifically notes that the electrodes are produced on the surface of the membrane. In fact, the Examiner recognizes in the rejection that Shahinpoor fails to disclose that the step of adsorbing metal complexes can be repeated. In the present invention, however, the repeated adsorption, in combination with the repeated reduction and washing steps, allows the metal to be deposited inside the resin product. As such, it is apparent that Shahinpoor does not teach deposition within the resin product, since Shahinpoor fails to even suggest the procedure through which this is accomplished in the present invention.

Moreover, Nidola fails to add any teachings to the deficiencies of Shahinpoor to render the present claims obvious. In particular, Nidola also merely teaches deposition of a metal coating on the surface of an ion-exchange resin membrane. Nothing in the Nidola reference teaches or suggests that the metal electrode can be deposited inside the resin product. In fact, Nidola specifically teaches away from deposition of the metal electrode inside the resin product at Col. 4, lines 65-68, where it is specifically noted that adsorption of the metal salts takes place mainly on the membrane surface and is a function of the contact time and temperature for a certain depth from the surface exposed to contact with the solution. Clearly, Nidola is merely teaching deposition of a metal on the surface of the resin, as opposed to inside the resin product. In fact, even where Nidola suggests repeating certain steps of the deposition, as noted by the Examiner at Col. 5, lines 13-14, and Col. 8, lines 42-43, this is accomplished for the goals of improving adherence between the deposited metal film and the membrane, and a reduction in electric resistivity between two laterally spaced points on the coating. Nidola fails in any way to recognize that repeatedly conducting the adsorption, deposition, and washing steps will increase the deposition of the metal inside the resin product, let alone that such effects will achieve an increase in bending and degree of displacement in the actuator.

The unique effects achieved through the present invention have been discussed by the present inventors through a paper entitled "Morphology of Electrodes and Bending Response of the Polymer Electrolyte Actuator", *Electrochimica Acta* 46 (2000) 737-743, as previously provided to the Examiner and attached hereto. The results set forth in the article demonstrate the unique advantages achieved through the present invention, in that the repeated steps increase the deposition of the metal to the inside of the resin product so as to provide improved bending and displacement. In fact, the results achieved through the present invention as set forth in the examples demonstrate that repeatedly conducting the sequence of adsorption, deposition, and washing exponentially changes the displacement of the actuator up to a certain number of processing steps.

The Examiner contends that it is generally known to regulate the amount of metal deposited by controlling specific parameters of processing, such as the number of cycles. However, the present invention is not merely concerned with regulating the amount of metal deposited, but is instead concerned with depositing the metal within the interior of the resin product. The prior art fails to recognize that repeatedly conducting each of the steps of adsorption, deposition, and washing will achieve such a continuous deposition of metal inside the resin product. Moreover, nothing in the teachings of these references recognizes that such an increase of metal deposited within the interior of the resin product will improve the bending or displacement of the actuator. In fact, as set forth, Nidola even indicates that adsorption of the salts is a function of contact time and temperature, specifically for deposition on the membrane surface. Nidola fails to even recognize that deposition can be controlled by repeating these sequential steps of adsorption, deposition, and washing, let alone that such steps result in deposition inside the resin product, as opposed to merely on the membrane surface. Also, merely depositing thicker layers of a metal on the surface does not achieve the present invention, which clearly requires deposition of the metal inside the resin product. Accordingly, the mere fact that certain steps of a deposition process may be repeated does not demonstrate that such prior art references suggest sequentially repeating an adsorption, deposition, and washing step to achieve deposition of the metal inside the resin product.

As shown in Fig. 5 of the *Electrochimica Acta* article, the repetition of the sequential steps to achieve deposition of the metal inside the resin product leads to an increase in the interfacial area between the ion-exchange resin product and the metal

electrode. The interfacial area can be regarded as the electrical double-layer capacitance in electrochemistry. The capacitance is increased by repeating the process steps of the present invention. When the capacitance is increased, the degree of displacement is increased. As such, when the interfacial area is increased, the degree of displacement is increased. As set forth in the attached paper, however, there is a limit to this increase in capacitance and displacement. In particular, once the metal is deposited to a certain degree within the interior of the resin product, the capacitance levels, and the deformation performance decreases. As such, there is an optimization in the number of sequential processing steps to achieve the deposition of the metal. Such optimization is clearly set forth in dependent claims 8 and 9, which disclose the number of cycles for repeating the sequential steps.

Accordingly, none of the prior art references discloses or suggests the process of the present invention, which involves repeatedly conducting the steps of adsorption, deposition, and washing, let alone such a process which results in an ion-exchange resin product having a metal electrode thickness ratio as claimed in the present invention. Accordingly, the rejection of claim 1 based on the combination of these references is improper. Withdrawal of the rejection based on these references is, therefore, respectfully requested.

In view of the above remarks, entry of the amendment, reconsideration and withdrawal of the rejection and favorable reconsideration are respectfully solicited.

Should the Examiner have any questions regarding any of this information, the Examiner is invited to contact Applicants' undersigned representative by telephone at 412-471-8815.

Respectfully submitted,

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Morphology of electrodes and bending response of the polymer electrolyte actuator

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Abstract

In order to induce bending motion in a perfluorinated polymer electrolyte by electric stimuli in water or saline solution, plating with metal is required. To fabricate electrodes, a perfluorocarboxylic acid membrane was soaked in Au(III) di-chloro phenanthroline complex solution, and then any adsorbed Au(III) cation complex was reduced in aqueous sodium sulfite. Optimizing the motion response depends on control of the chemical plating procedure. By sequential adsorption / reduction cycling, a suitable pair of gold electrodes with a fractal-like structure have been grown. This high interfacial area between the electrodes and polymer electrolyte leads to larger deformation. The measured deformation progressively improves with cycling. Displacement rates were proportional to current. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer electrolyte; Gold electrode; Polymer–metal composite; Micro machine; Soft actuator

1. Introduction

Micro-electro-mechanical devices can be made with current IC technology [1]. However, the technology is complex and expensive. Recently, considerable attention has been paid to actuators based on the deformation of polymer gels in response to environmental change [2]. These so-called mechano-chemical actuators convert chemical, thermal or photon energies into mechanical energy due to polarity change. These devices are simple and easy to design and fabricate. Soft actuator based on electro conductive polymer has been developed by several workers [3–5]. Conductive polymers such as polyaniline, polypyrrole, and polyacetylene can increase their electrical conductivity from the insulator to metallic regime upon the occurrence of certain chemical or electrochemical doping reactions. These reactions have been shown to be accompanied by a change in the volume of the polymer, such that the polymers can be manipulated to expand or contract.

Advances have been made with polymer electrolyte membranes plated with platinum, which deform under electric stimuli in water or saline solution [6–8]. These polymer electrolyte actuators (PEAs) have superior deformation, and quick response, but normally require substantial applied voltage to give sufficient deformation, and introduce electrolytic effects, e.g. gas production.

In the field of medical equipment and micro-robotics, there is great demand for a miniaturized, lightweight and flexible actuator. PEAs are particularly suitable for in vivo applications provided electrolysis is eliminated. The polymer electrolyte actuator effectively comprises a solid polymer electrolyte, at least two electrodes, coun-

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ter ions (e.g. H$^+$, Na$^+$), and any solvent present in-situ. The response of the PEA is controlled by many factors; not only the intrinsic properties of its components, but also the dimensions of the device, and details of the electrode-forming process.

Perfluorinated polymer electrolyte membranes in the carboxylic acid form are superior to the corresponding sulfonic acid form for this application. They have higher ion-exchange capacity and better mechanical strength. Gold is a promising material as electrode, being stable in acid, yet softer, more conductive, and less active in electrochemical reactions than platinum [9,10].

Previous papers [11,12] have proposed the deformation model of the PFAs, in which the deformation is attributed to the osmotic drag water flow associated with the capacitive current. The model successfully predicted the bending behavior of the solid polymer electrolyte membrane platinum composite, quantitatively. According to the model proposed, the amplitude of the deformation is proportional to the capacitive current and a transference coefficient of water. Hence, a high interfacial area between the electrodes and polymer electrolyte should lead to larger deformation [13,14]. Other factors conducting to good response are high electrode conductivity and efficient water transport as solvation sphere of the migrating cation, which ideally is highly hydrophilic, i.e. having a high 'osmotic drag' coefficient.

This report illustrates the advantage of optimizing the interfacial area between electrode and membrane to enhance deformation response with minimal electrolysis. To achieve this, gold deposits in the film are accumulated by sequential adsorption–reduction plating cycles. The morphology of the deposited electrode and the factors affecting the deformation performance are discussed.

2. Experimental

2.1. Preparation of the composite

Fig. 1 is a schematic representation of method for preparation of a gold–Flemion® composite. The Flemion® (Asahi Glass Co., Ltd.) is perfluoro carboxylic acid cation-exchange membrane with an ion-exchange capacity of 1.44 meq/g and 0.14 mm thick. After surface roughening by 'dry-blasting', both sides of the membrane, were chemically plated with gold as follows [9,10]. The perfluorocarboxylic acid membrane was soaked in Au(III) di-chloro phenanthroline complex solution for > 10 h at room temperature, rinsed, and then any adsorbed Au(III) cation complex in the membrane was reduced in aqueous sodium sulfite at 40–70°C for 6 h.

By sequential adsorption–reduction cycling up to 8 times, a suitable gold loading in the membrane may be accumulated. After washing the composite membrane in 4N HCl at 70°C, the membrane was immersed in 0.1N NaOH at room temperature for > 12 h to exchange to the sodium (Na$^+$) form.

2.2. Characterization of the composite membrane

The thickness of the gold layer electrode was measured by a fluorescent X-ray coating thickness gauge of SEIKO Industrial & Electronics, which has a dynamic response up to 5 μm. The surface resistance of the plated electrode was measured with a Kaise SK-6155 multi-meter. The composite was then cut into a ribbon with a width of 1 mm, and the resistance measured across a length of 7 mm. The interfacial area was evaluated by electric double layer capacitance determined from cyclic voltammetry (−0.5 to +0.5V) without reference electrode at a scan rate of 10 mV s^{-1} scan
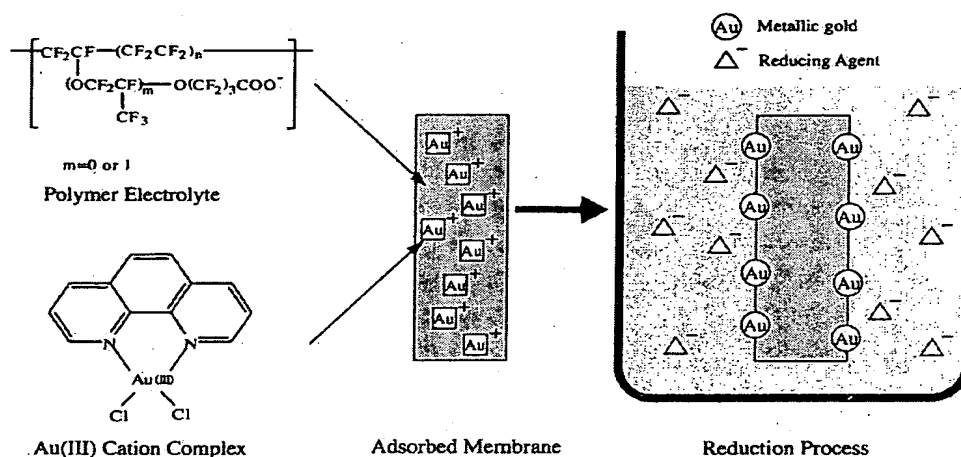

Fig. 1. Schematic representation of gold–solid polymer electrolyte composite prepared by adsorption–reduction method.
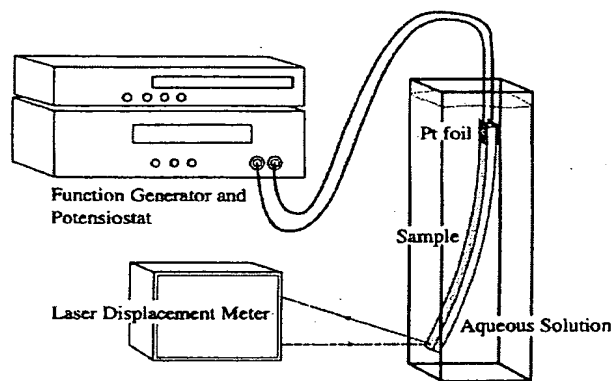
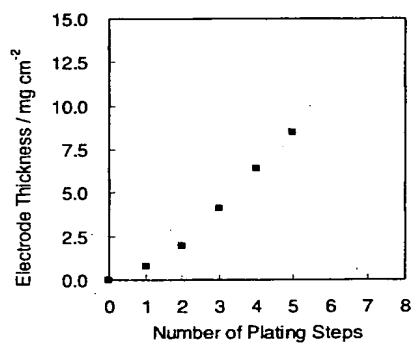Fig. 2. A schematic of displacement measuring system.

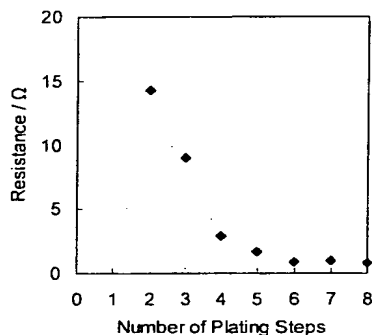Fig. 3. Electrode thickness of a single side in the membrane.

Fig. 4. Electrical resistance of the membrane surface ($L = 7$ mm) (sample size: 1.0×7.0 mm).

rate (Electrochemical Workstation BAS 100 B/W, Bio-analytical Systems, Inc.). The distribution of gold deposits in the membrane and their cross-sectional morphology were examined with scanning electron microscopy at 15 KV acceleration voltage (Hitachi SEM S-2500).

2.3. Deformation testing

Fig. 2 is a schematic of the set-up for evaluating bending response. The plated polymer electrolyte membrane was cut into a ribbon of 1 mm width and 8 mm length. The ribbon was supported vertically in water by clamping one end in platinum foil to make electrical contact with the gold electrode. Electric signals were supplied from a Yokogawa AG1200 waveform generator and a Hokuto Denko HA-501G potentiostat/galvanostat. Displacement of the free end at a distance of 5 mm from the fixed point was measured by a Keyence LC-2220/2100 laser displacement meter directed through the glass sample cell at room temperature.

The displacement response was stimulated by a square-wave and triangular-wave input signal (± 2.0 V) at a frequency of 0.1 Hz.

3. Results

3.1. Characterization of the composite membrane

3.1.1. Electrode thickness

Fig. 3 shows the development of electrode thickness in the plated membrane. By adsorption–reduction cycling, the thickness increases continuously with the number of plating steps, though it appears that the ion exchange capacity is unaffected by progressive accumulation of Au deposits.

3.1.2. Surface resistance of electrode

Fig. 4 shows the drop in surface resistance of the electrode with plating sequence. A working value of < 3 Ω (sample size: 1×7 mm) was typically reached after 4 plating cycles.

3.1.3. Interfacial area between ion exchange polymer and the electrode deposit

Fig. 5 shows SEM micrographs of the cross section of the composite membrane. By adsorption–reduction cycling, a fractal-like structure of gold with high interfacial area within the membrane is obtained. The membrane structure depends on the conditions of plating and surface-roughening pre-treatment. The distribution of gold in the membrane is very sensitive to the reduction condition.

The interfacial area can be evaluated because it is proportional to be electric double-layer capacitance, which can be measured easily. Fig. 6 shows a representative cyclic voltammogram of the membrane in water. Electrode potential was cycled within the double-layer charging region (-0.5 to $+0.5$ V), and the scan rate was 10 mV s^{-1}. In the absence of electrochemistry, the double-layer capacitance is the ratio of current to voltage scan rate. Fig. 7 shows the trend in the capaci-
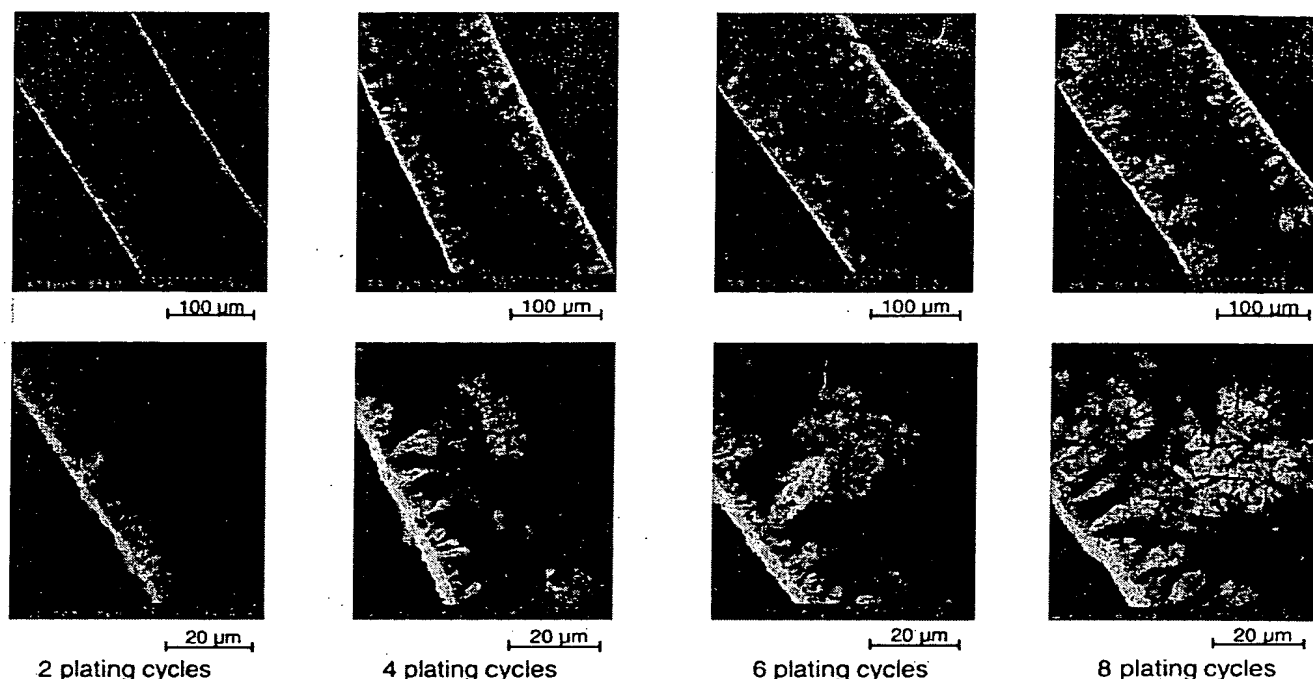
2 plating cycles   4 plating cycles   6 plating cycles   8 plating cycles

Fig. 5. SEM micrograghs in cross-section of membrane electrode.

tance of the membrane with plating cycle. To check reproducibility, the data for two samples is illustrated. Both show a systematic increase in capacitance up to ∼ 6 or 7 plating cycles but with a clear approach to a limiting value or saturation.

3.2. Analysis of the deformation

Fig. 8 shows the effect of plating cycles on peak-to-peak displacement of the composite membrane (Na^+-form) on applying a 2 V square wave at 0.1 Hz. The displacement increased with the number of plating cycles up to roughly 6 times, but showed no clear im-
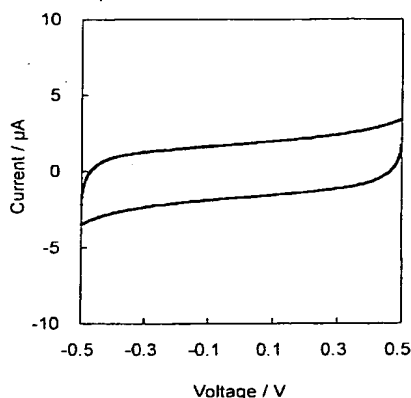
provement beyond. The interfacial area begins to decrease and/or the hardness of the electrode increases with excessive plating, thus becoming deleterious for performance.

Fig. 9 shows the development of displacement with electric double layer capacitance. The capacitance increased the displacement proportionally except plot of 462 μF cm^{-2}. The displacement at the plot was given low value caused of high resistance with electrodes.

Fig. 10 shows the waveforms of current and displacement response of the composite membrane (Na^+-form) at 2 V applied as a triangular wave-form at 0.1 Hz. At region A, some kind of redox current and the increase in the slope of the displacement was observed. At other regions during the sweep of voltage, the

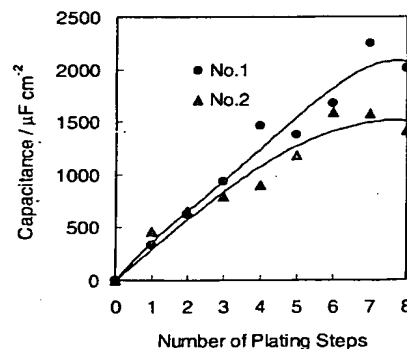Fig. 6. Cyclic voltammogram of the composite in water.
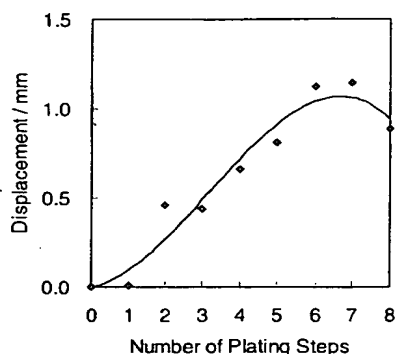

Fig. 7. Electric double layer capacitance.

Fig. 8. Peak to peak displacement of the composite membrane driven by 2 V square-wave vs. number of plating steps.
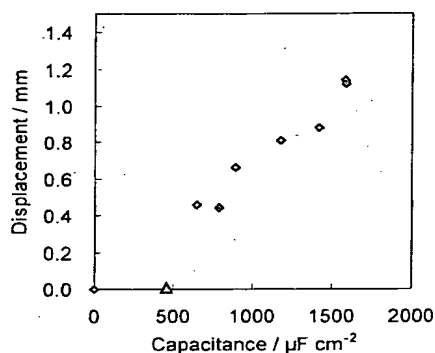

Fig. 9. Displacement vs. electric double layer.

capacitive current was only observed and the displacement linearly increased with time.

Fig. 11 shows the trend in displacement rate with increasing current at point **B**, as described in Fig. 10.
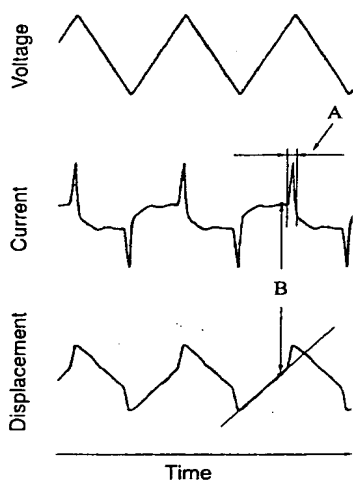

Fig. 10. Waveforms of voltage, current and displacement of membrane. A: electrolysis range; B: maximum current value with no-electrolysis.

After the first plating $(n = 1)$, It is impossible to measure displacement rate and current because the resistance of the electrode surface is still extremely high.

It is clearly seen that displacement rate is proportional to current, i.e. $d = kI$, where $d =$ displacement rate and k is a proportionality constant. This result is in conformity with the response model proposed in the previous paper. It can also be seen that k progressively drops with plating cycle number (n). Fig. 12 shows that the drop in k is actually proportional to n. Thus, there is a trade-off between amplitude of response (see Fig. 8) and speed of response (Fig. 11) at a given applied voltage and plating degree. The likely factor working against increasing displacement with plating cycle is a concomitant increase in rigidity of the composite with accumulating Au deposition. This result can also be explained by the previously proposed response model.

4. Discussion

The purpose of the sequential plating process presented in this paper is to explore electrode-forming processes of the PEAs with larger deformation. Increasing the number of plating steps results in a decrease in the surface resistance R_s, an increases in the double layer capacitance C_d, and an increase in the rigidity of the composite, k. The value of R_s decreases, sharply, by five plating cycles, and after that, it remains almost constant $(R_s = 1 \ \Omega)$. Deformation for the composites of 1 plating cycles was not observed, because of the high surface resistivity. Hence, the plating electrode requires more than 4 chemical plating cycles in order to significantly affect surface resistance.

Regarding the rigidity of the composite, the increase in the plating cycles is a disadvantage for larger deformations (Fig. 12). The increase in the double layer capacitance means an increase in the capacitive current. Growing the fractal-like structure of the deposited electrode by the sequential plating as shown in Fig. 5 is important for increasing the values of the double layer capacitance. The large increase in the capacitive current by the growth of the structure leads to larger deformation as the plating cycles, compensating for the negative effect of the rigidity of the composite. However, at eight plating cycles, the fractal-like structure has never been grown, and the double layer capacitance is almost the same as that of seven plating cycles (Fig. 7). Hence, the deformation performance of the composite of eight plating cycles is worse than that of 7 plating cycles as shown in Fig. 8, because of the rigidity of the composite. In consideration of all factors mentioned above, more than 4 plating cycles are needed and six–seven plating cycles are optimum for largest deformation of
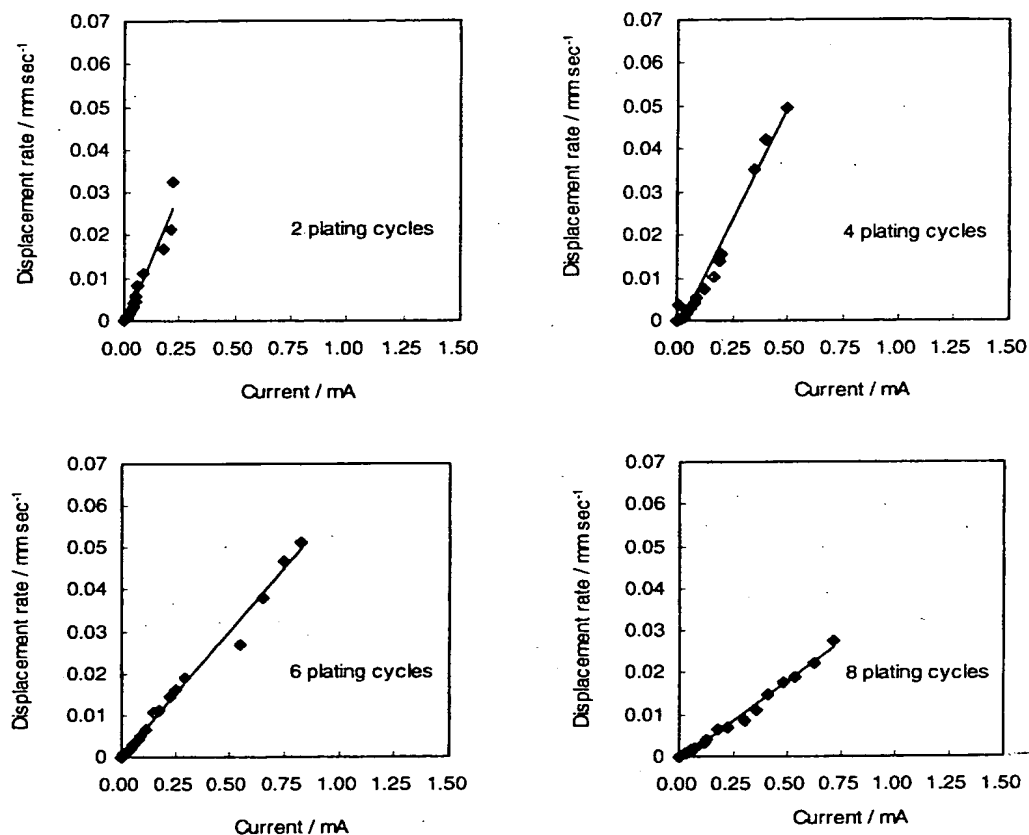
Fig. 11. Displacement rate vs. current.

the PFAs based on the perfluorocarboxylic acid membrane and Au composite.

The methods of forming solid polymer electrolyte membranes (SPM)/metal composites have been originally developed for using the composites as water electrolysis processes [15]. Two different plating methods, known as 'reductant permeation' (RP) [16] and 'impregnation-reduction' (IR) [17], have been developed

Fig. 12. Proportional coefficient vs. number of plating cycles.

for direct contacting of a polymer electrolyte membrane and a metal electrodes under wet conditions. For optimum performance of the PFAs, the metal-plating step should satisfy several criteria, namely, a low surface resistance of plated electrode, a high interfacial area, a wide potential window, and a low rigidity. Some properties of the plated electrode for the water-electrolysis do not meet the criteria. The sequential plating of gold presented in this paper is one of the answers to this problem.

In the near future, the effect of counter ion (Li^+, Na^+, K^+) must be investigated as an important part of the method optimization.

5. Conclusion

In electrode development, a sequential plating (adsorption–reduction) procedure has been shown to greatly improve the actuator displacement by build-up of fractal-like gold deposits which provide a high electrode/membrane interfacial area. The progressive deposition of high specific area improves the absolute
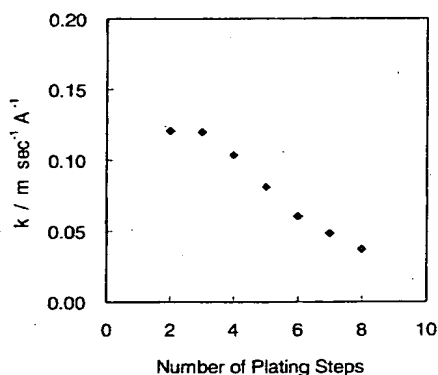
displacement with electrical stimulus over many plating cycles. The plating method must be improved by increasing the surface-to-volume ratio, or 'dispersion', of Au particles. The speed of response is proportional to the induced current, which is in turn a systematic function of plating cycle number. However, an optimum number of plating cycles (~ 6–7) is reached, beyond which little improvement in displacement occurs. Together with a gradual loss in speed of response, these effects suggest a deleterious increase in mechanical resistance or stiffness with excessive accumulation of gold.

Acknowledgements

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